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Quartz Crystal Microbalance Sensor for Organic Vapor Detection Based on Silica-Based Mesoporous Organic-Inorganic Hybrids

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Abstract:
Silica-based mesoporous organic-inorganic hybrid materials have examined for their ability to detect vapors of small organic molecules with high sensitivity and selectivity. Mesoporous SBA-15 serves as an inorganic host with high specific surface area, facilitating gas adsorption, and thus leads to highly sensitive response; while the presence of organic functional groups contributes to the greatly improved specific sensing property. The behavior of the tailor-made sensing materials is characterized by quartz crystal microbalance (QCM) transducer. In this mini review, we report two high-performance QCM-based sensors in the application of nerve agent and formaldehyde detection. Hydrogen-bond acidic functional groups and amine were grafted onto SBA-15, respectively. Both of the sensors exhibited high sensitivity and selectivity to the vapor analyzed, with a ppb-level detection limit.

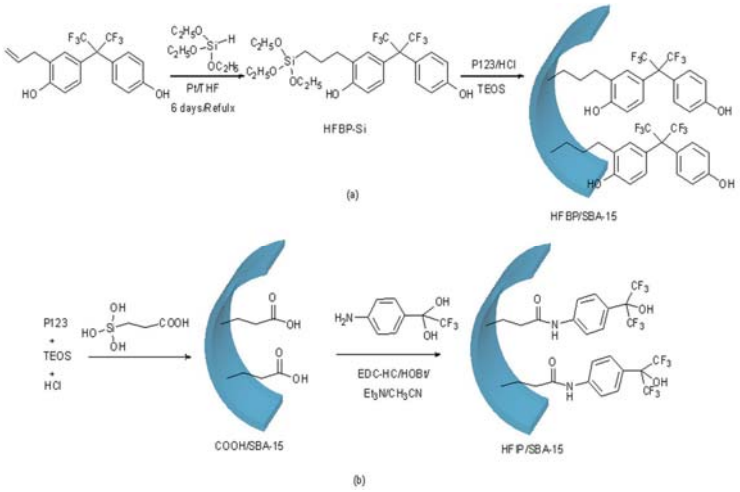
Key words: mesoporous organic-inorganic hybrid materials, nerve agent and formaldehyde detection, quartz crystal microbalance (QCM), gas sensor

Introduction

With the ever increased concern of homeland security and health, numerous attentions have been paid to the detection of both chemical warfare agents and indoor air pollutants. Organophosphorus compounds, such as Sarin, are recognized as one of the most toxic warfare agents. Carbon nanotubes[1], metal oxides[2], and hydrogen-bond acidic polymers[3], etc. have been reported to construct nerve agent detectors. The as-fabricated sensors can achieve high sensitivity and selectivity, however, there are still critical limitations of their practical application either in terms of long response–recovery time or the complexity associated with device fabrication. Formaldehyde is a probable human carcinogen, an allergen, and an intense irritant of eyes and mucous membranes and is therefore highly problematic as an indoor pollutant.[4] Though there are numerous methods for detecting and measuring gaseous formaldehyde, the past analytical approaches not only needed relatively expensive instrumentation, but also the pre-treatment methods are generally relatively slow (typically >30 min), often cumbersome and multistep, and frequently lack sensitivity. Therefore, there remains a pressing need for the development of high-performance nerve agent and formaldehyde gas sensors with high convenience.

For sorption-based sensors, active materials play a crucial role in improving overall performances. Silica-based mesoporous organic-inorganic hybrids are regarded as ideal candidates in the area of chemical sensing. The large surface area and uniform pore size are beneficial for rapid molecular diffusion, leading to enhanced sensitivity[5]; while the good thermal and chemical stability[6] enables relative stable sensing properties. The abundant silanol groups in the framework made mesoporous silicas great hosts for incorporating various organic groups, so that tailor-made active materials could be designed to achieve specific molecular detecting. In this context, the organic–inorganic mesoporous silicas serve as powerful sensing materials to achieve highly sensitive, stable and selective gas detection.

In this paper, two mesoporous hybrids were reported featuring hydrogen-bond acidic groups and amine to achieve high-performance sensing properties toward warfare agents[7] and formaldehyde [8], respectively. Hydrogen-bond acidic functional groups, such as fluoroalcohol and fluorinated-phenol derivatives were adopted into silica framework due to its strong H-bonding interactions between the acid moieties of the



Scheme 1 The synthesis of the functionalized mesoporous hybrid material (a) HFBP/SBA-15 and (b) HFIP/SBA-15.

structure and the oxygen atoms of organophosphate esters.[3] On the other hand, considering the specific reaction between the -NH_2 group and formaldehyde, amine functionalized mesoporous silicas were designed to construct formaldehyde sensors. The sensing properties of as-made hybrids were characterized by quartz crystal microbalance (QCM) transducers. QCM has been widely used in transducer technology for real-time measurements along with the conveniences of portability, low cost, and ease of operation. Our experiments show that QCM sensors based on hb derivatives and amine functionalized mesoporous silicas have excellent sensitivity, selectivity, short response–recovery time as well as high convenience toward nerve agent and formaldehyde, respectively.

QCM Sensors for DMMP Vapor based on Fluoroalcohol and Fluorinated-Phenol Derivatives Functionalized SBA-15

We report the synthesis of fluorinated-alcohol and fluorinated-phenol derivatives modified mesoporous SBA-15/ organic hybrids via a co-condensation route. (see Scheme 1) Hexafluorobisphenol (HFBP) and hexafluoroisopropanol (HFIP) were grafted onto mesostructured silica, respectively. These hybrids combined the advantages of the abundant active sites from the large specific area of SBA-15 and the specific interaction with analytes arising from hb acidic functional groups.

The microstructure of the hybrids was determined by small-angle X-ray scattering (SAXS) experiments, N_2 porosimetry, and transmission electron microscopy (TEM). (see Fig.1 and Fig.2)

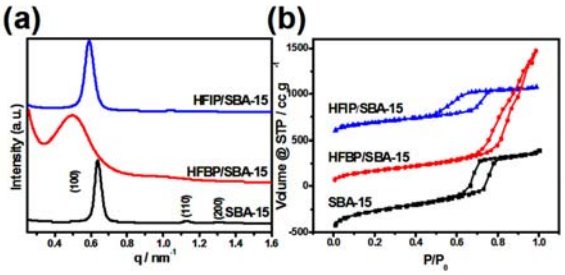


Fig. 1. (a) Small angle X-ray Scattering patterns and (b) N_2 adsorption isotherms of the different mesoporous samples.

All the samples exhibit strong diffraction peaks typical of SBA-15 structure. All the corresponding isotherms in N_2 adsorption-desorption experiment can be identified as the type IV-shaped isotherm according to the IUPAC classification, which is typical for mesoporous solids with uniform size distributions. The type H3 hysteresis loop of HFBP/SBA-15 indicates the slit-shaped mesopores, while the presence of H1-type hysteresis loops in the HFIP/SBA-15 sample implies the existence of open-ended cylindrical mesopores, which are in agreement with the results of the TEM image (Fig. 2).

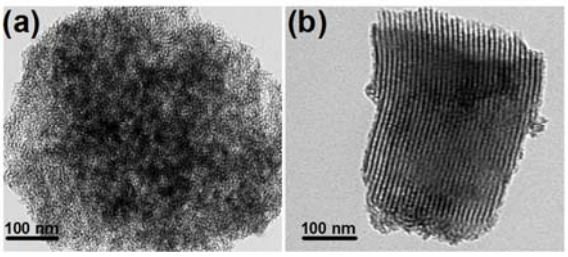


Fig. 2. TEM images of the hybrids HFBP/SBA-15 (a) and HFIP/SBA- 15 (b)

The presence of fluoroalcohol and fluorinated-phenol derivatives associated with the SBA-15 material was confirmed by FT-IR (Fig. 3).

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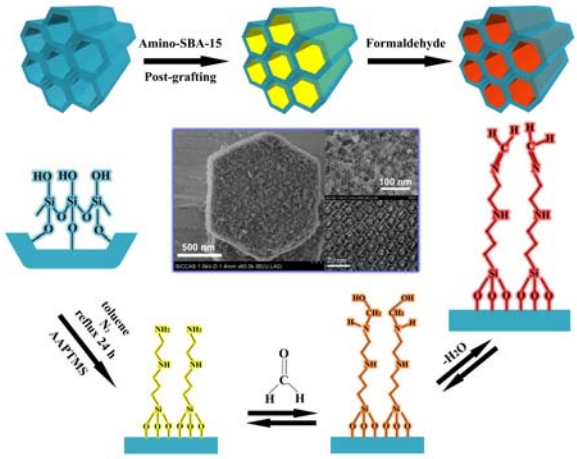

Scheme 2. Scheme of the synthesis process of the amine groups functionalized on inner wall of uniform hexagonal lamelliform mesoporous SBA-15 and specific capturing mechanism to formaldehyde-molecules.

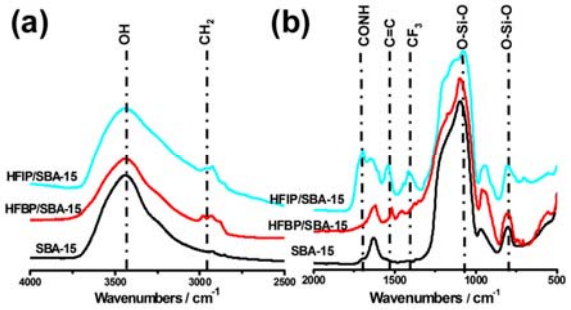

Fig. 3. FT-IR spectra of SBA-15, HFBP/SBA-15 and HFIP/SBA-15

Responses of as-made hybrids to dimethyl methylphosphonate (DMMP), a simulant for the class of chemical warfare agents, were investigated by a QCM transducer. According to the results of the sensing experiments, the chemical sensors based on HFBP/SBA-15 and HFIP/SBA-15 hybrids were highly sensitive and selective toward DMMP. (Fig. 5 and Fig. 6)

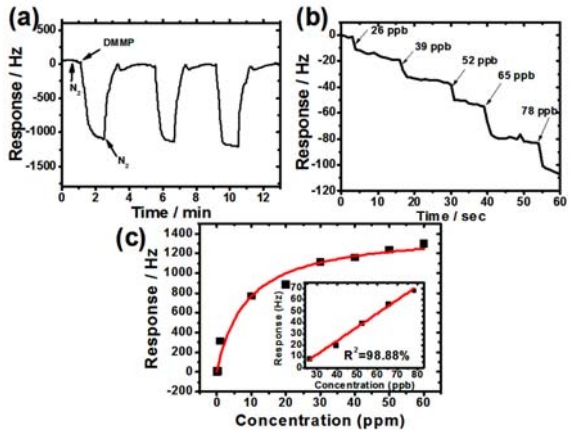

Fig. 5 (a) Short-term repeatable and reversible rapid sensing response of the HFBP/SBA-15 coated QCM sensor to 60 ppm DMMP vapour. (b) Real-time response curves of the sensor upon exposure to different concentrations of DMMP vapour ranging from 26 ppb to 78 ppb. (c) Sensing response vs. the DMMP concentration.

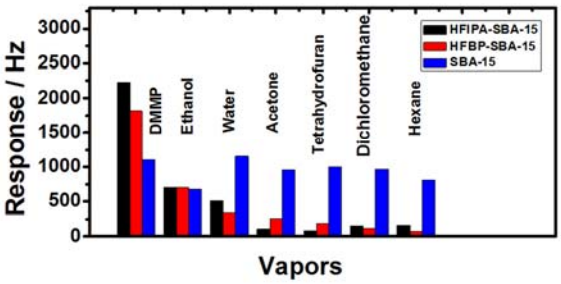

Fig. 6 Frequency change of the sensors based on hb groups functionalized SBA-15 and pristine SBA-15 in response to saturated common organic solvents and 130 ppm DMMP vapour at room temperature.

QCM Sensors for Formaldehyde based on Amine Functionalized SBA-15

Well-defined mesostructured and uniform hexagonal lamelliform functionalized SBA-15 with a homogeneous layer and desired loadings of amine functional groups inside the pores was prepared using a post-grafting route. The as-synthesized hybrids were characterized by various standard techniques. The results show that hexagonal lamelliform SBA-15 with a uniform particle size and short vertical channels plays two significant roles in uniformly dispersing amine functionalizing groups and effectively adjusting the loadings of the functional groups within the mesopore channels. The TEM (Fig. 7) investigation provides direct observation of the pore structures and distribution of amine groups in the NH2-SBA-15 composite.

Figure 8a shows the sensing properties of the NH_2-SBA-15 coated QCM sensor toward formaldehyde vapor. The advantages of the resultant materials were demonstrated by faster adsorption rates and larger adsorption capabilities toward formaldehyde molecules, in comparison to conventional SBA-15. Experiment results indicated that the chemosensor had high sensitivity and good chemoselectivity to formaldehyde vapor, with a ppb-level detection

limit. The excellent sensing results in this study indicate that the amine-functionalized mesoporous silica SBA-15 is promising in nose-on-a-chip applications.

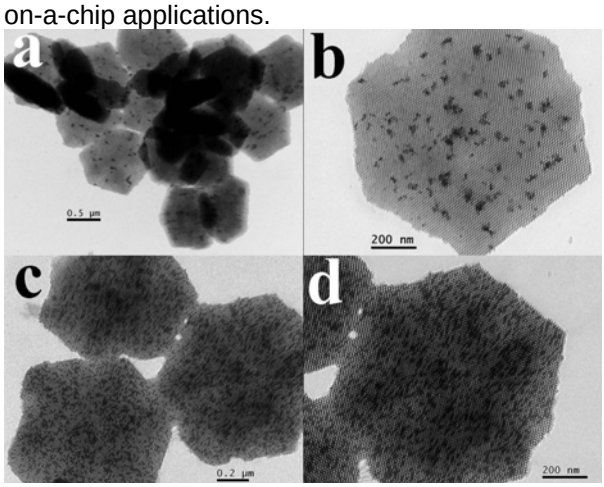

Fig.7. TEM images corresponding to as-synthesized amine-functionalized SBA-15 with desired loadings (a, b NH_2-SBA-15-1; c, d NH_2-SBA-15-2: the images are clearly show that uniform and highly dispersed amine groups in the hexagonal channels of SBA-15.

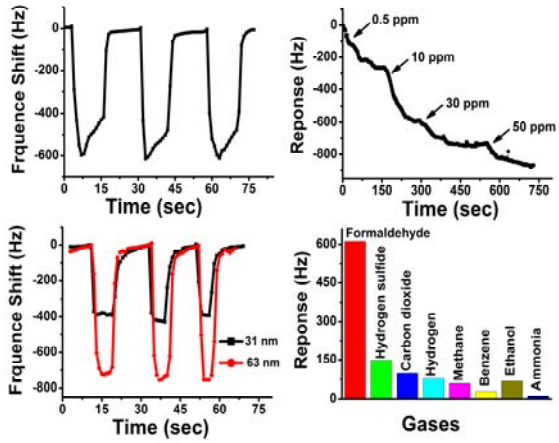

Figure 8. (a): Short-term repeatable and reversible rapid sensing response to 50 ppm formaldehyde vapor. (b): After 45 days, the same sensor response to 50 ppm formaldehyde vapor (c): Typical sensor responses versus formaldehyde of various concentrations of o.5, 10, 30 and 50 ppm. (d): The resonant frequency shift increased with increasing thickness of the amine-SBA-15. (e): Response of the formaldehyde sensor to various kinds of interfering gases compared with that of 50 ppm formaldehyde

Conclusion

In this review, we reported two chemical sensors toward warfare agent and formaldehyde, respectively. Both of them exhibited the parts-per-billion sensing level. Besides, the materials also exhibit remarkably enhanced selectivity compared with pristine SBA-15 due to specific interaction between the analytes and organic functional group. These results suggest that high sensing performances, along with low cost of organic-inorganic mesoporous hybrids coated QCM devices are very promising in the application of gas sensing. Besides, rational design of functionalized mesoporous hybrids seems to be a very desirable strategy to construct tailor-made chemical sensors for different analytical demands.

Acknowledgements

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